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July 29, 2020

Dr. Souad Benromdhane
Environmental Protection Agency
Research Triangle Park
109 T.W. Alexander Drive
Mail Code C539-07
Research Triangle Park, NC 27709

RE: Petition for VOC Exemption for HCFO-1224yd(Z)

Dear Dr. Benromdhane:

AGC Chemicals Americas, Inc. ("AGC") requests the U.S. Environmental Protection Agency ("EPA") to exempt the chemical (Z)-1-chloro-2,3,3,3-tetrafluoropropene ("HCFO-1224yd(Z)") (CAS No. 111512-60-8) from EPA's definition of a volatile organic compound ("VOC"). Exclusion from the definition of a VOC would allow HCFO-1224yd(Z) to be used within the United States without being considered to be a precursor to the formation of tropospheric ozone.[1]

As described in the attached petition, HCFO-1224yd(Z) has a very low potential to contribute to the formation of ozone in the troposphere. When ozone impacts are measured on a mass basis, HCFO-1224yd(Z) is estimated to be around 5% as impactful as ethane. In addition, while the (E) isomer of HCFO-1224yd is more reactive, the isomer is still around 10% of the value attributable to ethane.[2] Given this negligible reactivity, HCFO-1224yd(Z) offers significant benefits for reducing ozone formation, especially when consideration is given to existing chemicals designed for the same end uses.

In accordance with applicable EPA policy, we have calculated the maximum incremental reactivity ("MIR") of HCFO-12234yd(Z) and the Maximum Ozone Incremental Reactivity ("MOIR"). This report also includes calculation of another measure of reactivity, Equal Benefits Incremental Reactivity ("EBIR"), which shows similar results.[3] Given these calculated values, EPA may approve HCFO1224yd(Z) on the basis of its comparison to the reactivity of ethane alone.

[1] *See* 40 C.F.R. §51.100(s).

[2] The (E) isomer in any event constitutes 2% or less of HCFO-1224yd(Z).

[3] The EBIR of HCFO-1224yd(Z) has been calculated to be 0.033±0.006. This compares with an EBIR of ethane of 0.14±0.04.

The attached petition for HCFO-1224yd(Z), however, also addresses several factors that EPA has historically reviewed as part of the Agency's VOC exemption process in order to ensure protection of human health and the environment. To summarize information regarding these factors:

(1) The use of HCFO-1224yd(Z) as a refrigerant means that the compound will not be generally emitted into the atmosphere on a continuous basis in significant amounts. Rather, equipment will be initially charged and then serviced with HCFO-1224yd(Z) with minimal losses of refrigerant to the atmosphere over time, subject to EPA regulations concerning servicing and "venting."

(2) HCFO-1224yd(Z) also has a very low ozone depletion potential ("ODP") and thus is very unlikely to contribute to ozone depletion in the stratosphere. HCFO-1224yd(Z) has been approved by EPA as an acceptable substitute for use in new and retrofitted centrifugal chillers, positive displacement chillers and industrial process refrigeration.[4]

(3) The global warming potential ("GWP") of HCFO-1224yd(Z) is approximately 1, or roughly equivalent or less than that of carbon dioxide. HCFO-1224yd(Z) is also relatively short-lived in the atmosphere, with a lifetime of approximately 20 days.

(4) HCFO-1224yd(Z) has low toxicity, with a No Adverse Effects Concentration (NOAEC) of 10,000 ppm based on the results of a 90-day inhalation study reviewed by EPA.

We understand that the Agency has many competing priorities, but would urge your prompt attention to the attached petition. Please let us know if you need any additional information regarding our analysis of HCFO-1224yd(Z). We would be pleased to accommodate any further inquiries.

Sincerely

/s/ Robert J. Meyers
Robert J. Meyers
On Behalf of
AGC Chemicals Americas, Inc.

cc: Anne Idsal, Acting Assistant Administrator, Office of Air and Radiation
Peter Tsirigotis, Director, Office of Air Quality Planning and Standards

[4] 84 Fed. Reg. 64,765 (Nov. 25, 2019).

Petition for VOC Exemption

HCFO-1233yd(Z)

AGC Chemicals Americas, Inc

July 29, 2020

I. Introduction

AGC Chemicals Americas, Inc. ("AGC") has been approved by EPA to introduce HCFO-1224yd(Z) for use in the United States for certain defined end uses in refrigeration and air conditioning.[5] In this petition, AGC seeks a determination by EPA that HCFO-1224yz(Z) has negligible photochemical reactivity and requests that EPA add HCFO-1224yd(Z) to the list of chemical compounds that EPA has determined are excluded from the definition of a volatile organic chemical ("VOC").[6]

In support of this petition, we are attaching a recent report authored by Dr. William P.L. Carter.[7] The findings of this report are described in more detail below, but Dr. Carter's analysis of HCFO-1224yd(Z) shows that the reactivity of this chemical, including its (E) isomer, is far below that of ethane, the benchmark that EPA has typically used to determine whether VOCs can be considered to have negligible photochemical reactivity. Furthermore, the attached analysis indicates that any uncertainties regarding the ozone formation impacts of HCFO-1224yd(Z) are "estimated to be small compared to variability in atmospheric conditions."[8]

This petition also addresses other health and environmental impacts that EPA has traditionally reviewed in determining whether to exclude a chemical compound from the regulatory definition of a VOC. As outlined in more detail below, HCFO-1224yd(Z) has an extremely low potential to contribute to ozone depletion, a low Global Warming Potential ("GWP") and low toxicity, with a No Adverse Effects Concentration (NOAEC) of 10,000 ppm. Thus, HCFO-1224yd(Z) fits well within the parameters of other chemical compounds that EPA has previously determined to be exempt from the definition of a VOC, in accordance applicable guidance documents. We respectfully request EPA's prompt review and action on this petition.

II. HCFO-1224yd(Z) Possesses Negligible Photochemical Reactivity

A. All Calculated Reactivity Values for HCFO-1224yd(Z) Are Well Below Those of Ethane

As demonstrated by the chart below, the "best estimate" of the incremental reactivity of HCFO-1244yd(Z) demonstrates that calculated values are well below that of ethane. When measured

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[5] 84 Fed. Reg. 64,765 (Nov. 25, 2019).

[6] 40 C.F.R. §51.100(s)(1).

[7] Estimation of the Ground-Level Atmospheric Ozone Formation Potential of Isomers of 1-Chloro-2,3,3,3-Tetrafluoro 1-Propene HCFO-1224YD, Attachment 1.

[8] *Id.* at 1.

with respect to Maximum Incremental Reactivity ("MIR"), both HCFO-1224yd(Z) and its (E) isomer are a fraction of the MIR of ethane, *i.e.*, 0.052 and 0.086 gm O_3/gm VOC as compared with 0.29 gm O_3/gm VOC for ethane. The error margins for the MIR calculations do not change this assessment.

This same result is obtained for both HCFO-1224yd(Z) and the (E) isomer under calculations performed for Maximum Ozone Incremental Reactivity ("MOIR") and Equal Benefits Incremental Reactivity ("EBIR"). Again, all calculations show that HCFO-1224yd(Z) and its (E) isomer should be considered to have negligible photochemical reactivity.

Table 2. Incremental reactivities calculated for HFCO-1224yd(Z), ethane, and the base ROG mixture in the MIR, MOIR, EBIR, and base case scales.

Compound or Mixture	Incremental Reactivity (gm O_3 / gm VOC)			
	MIR	MOIR	EBIR	Base
Ambient ROG Mixture [a]	3.9±0.6	1.5±0.3	0.9±0.2	1.21±0.45
Ethane	0.29±0.07	0.20±0.05	0.14±0.04	0.17±0.04
HFCO-1224yd(Z)				
$Y_{Nitrate} = 0$	0.055±0.011	0.045±0.008	0.036±0.006	0.039±0.007
$Y_{Nitrate} = 5\%$	0.049±0.010	0.039±0.007	0.029±0.006	0.033±0.006
"Best Estimate" (average)	0.052±0.010	0.042±0.008	0.033±0.006	0.036±0.006
HFCO-1224yd(E)				
$Y_{Nitrate} = 0$	0.091±0.015	0.073±0.012	0.080±0.013	0.118±0.022
$Y_{Nitrate} = 5\%$	0.081±0.015	0.060±0.011	0.068±0.013	0.104±0.021
"Best Estimate" (average)	0.086±0.015	0.067±0.012	0.074±0.013	0.111±0.022
Reactivity Ratios (mass basis) [a]				
HFCO-1224yd(Z) / Ethane	0.19±0.02	0.22±0.04	0.24±0.05	0.23±0.04
HFCO-1224yd(E) / Ethane	0.31±0.04	0.35±0.07	0.55±0.15	0.71±0.20

[a] Averages of ratios of HCFO/Ethane reactivities for each individual scenario.

This conclusion is additionally supported by the graphic below which plots MIR, MOIR and EBIR estimates for HCFO-1224yd(Z) and the E-isomer with respect to different atmospheric scenarios. In 39 different single-day scenarios, the calculated reactivity of HCFO-1224yd(Z) and the (E) isomer remains in all cases below that of ethane, even assuming different nitrate yields in the ozone-forming mechanism.[9]

[9] It should be noted that even varying nitrate in the various scenarios, the estimated uncertainty in the calculated values is approximately 15%. *Id.* at 8.

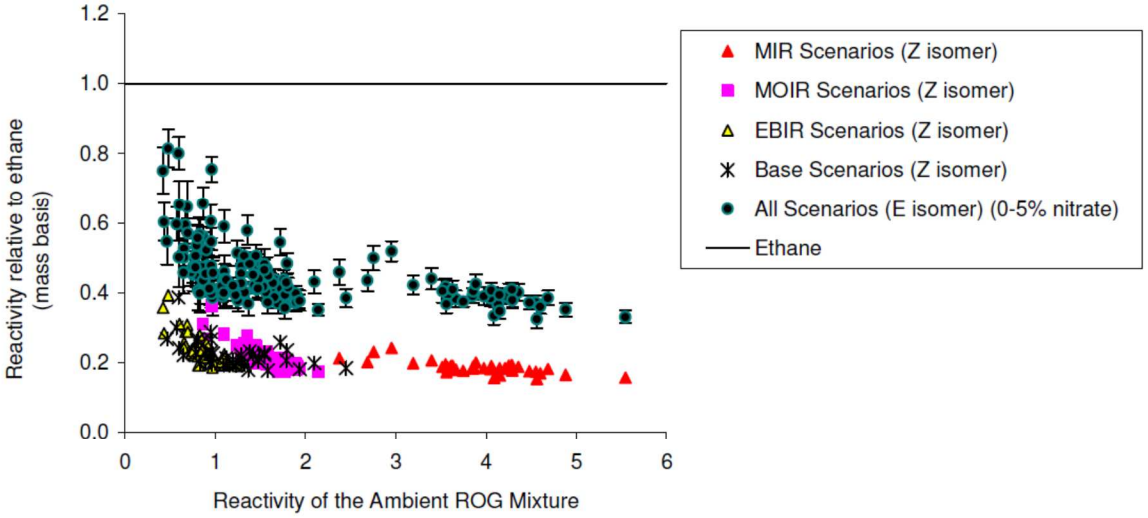

Figure 1. Plots of incremental reactivities of the HFCO-1224yd isomers relative to ethane for the individual scenarios against the incremental reactivity of the ambient reactive organic gas (ROG) mixture .

After evaluating all of the reactivity estimates regarding HCFO-1224yd(Z), the analysis attached to this petition concludes that:

> The ozone impacts of . . . HCFO-1224yd(Z) on a mass basis are estimated to be approximately . . . 5% of that of ethane . . . . The (E) isomer is more reactive, but still has an impact only about 10% that of ethane . . . It is clear that both of these compounds meet [the] ethane standard, assuming that the estimated mechanisms for these compounds are not significantly in error. [10]

Thus, policies that EPA has established with regard to the control of VOCs within state implementation plans have been addressed.[11]

B. Additional Factors Demonstrate HCFO-1224yd(Z) Will Not Significantly Contribute to Tropospheric Ozone Formation

In assessing whether a substance will contribute to ozone formation, EPA may also consider the end use of a substance and the relative quantity of the substance that will be used and/or emitted. In this regard, it is instructive that HCFO-1224yd(Z) has been approved by EPA under the Significant New Alternatives Program ("SNAP") for use in new and retrofit centrifugal chillers, positive displacement chillers and industrial process refrigeration.[12] This end use involves the charging of new and retrofitted equipment and maintaining proper charge levels over time, but

[10] Carter at 11.
[11] 42 Fed. Reg. 35,314 (July 8, 1977); 70 Fed. Reg. 54,046 (Sept. 13, 2005).
[12] 84 Fed. Reg. 64,765, 64,766 (Nov. 25, 2019).

does not involve direct "emissive" uses of HCFO-1224yd(Z) such as those that might occur through use of the substance in a consumer product.[13]

Apart from its low reactivity in the atmosphere, the ability of HCFO-1224yd(Z) to contribute to tropospheric ozone formation is constrained by how it will be produced and used in the "real world." Amounts of HFCO-1224yd(Z) that will be produced are not infinite; production amounts directed to the United States will be determined by the size of the market for SNAP-approved refrigeration end uses. And actual use of the product will be constrained by conditions and regulations imposed by EPA. Therefore, there is exceedingly little prospect that use of HCFO-1224yd(Z) will occur in amounts sufficient to influence the local formation of ozone.

In addition, while there uncertainties inherent in any prediction with regard to how ozone will form in different locations during different times of the year, the Carter study indicated these uncertainties are not great and would not significantly impact the analysis' conclusions on reactivity:

> Uncertainties in mechanisms of the individual VOCs are obviously the most important in affecting predictions of their ozone impacts. However, in the case of the HCFO-1224yd(Z) isomers the uncertainties do not appear to be large, and the major reaction pathway appears to be insensitive to uncertainties identified in the mechanism except for the nitrate yields from peroxy reactions, and the effects of this uncertainty is found to be relatively small compared to scenario-to-scenario variability.
>
> The main uncertainty in the case of the HCFO-1224yd isomers and related compounds is the fact that although we think we understand their atmospheric reaction mechanisms, their predictive capabilities have not been experimentally evaluated. However, there are experimental data concerning the chemically similar compounds 1,3,3,3-tetrafluoropropene, 2,3,3-Tetraflurorpropene, and trans 1-chloro-3,3,3-trifluoropropene propene (Carter 2009a-c), whose estimated mechanisms are very similar . . . [t]his suggests that the effects of the uncertainties in the mechanism for [HCFO-1224yd(Z) and (E) isomer] are probably small compared to effects of variabilities in atmospheric conditions . . . .[14]

Thus, additional factors, apart from the direct comparison of HCFO-1224yd(Z) to ethane, support a determination that the compound should be considered VOC-exempt.

III. HCFO-1224yd(Z) Also Addresses Considerations EPA Has Previously Reviewed Regarding Risk to Human Health or the Environment

EPA has indicated that "in general, VOC exemption decisions will continue to be based solely on consideration of the compound's contribution to ozone formation. However, if the Agency

[13] Knowing venting or release of HCFO-1224yd(Z) is also limited by Clean Air Act section 608(c) and 40 C.F.R. 82.154(a)(1). *Id.* at 64,766.

[14] *Id*. at 10.

determines that a particular VOC exemption is likely to result in a significant increase in the use of a compound and that the increased use would pose a significant risk to human health or the environment that would not be addressed adequately by existing programs or policies, EPA reserves the right to exercise its judgment in deciding whether to grant an exemption."[15] Based on the information provided below, there is no basis to conclude that utilization of HCFO-1224yd(Z) would significantly contribute to the formation of ozone or pose a significant risk to human health or the environment as described in EPA guidance documents and past Agency determinations concerning other VOC exemptions.

A. Contribution to Stratospheric Ozone Depletion

HCFO-1224yd(Z) has an ozone depletion potential ("ODP") of approximately 0.00012.[16] Thus, the effect of HCFO-1224yd(Z) on the stratospheric ozone layer is miniscule, especially in comparison to many other substances that are currently in use in the United States. The ODP of HCFO-1224yd(Z) is also significantly below the ODP of many substitutes that EPA has approved through the SNAP program.[17] Given EPA's recent approval of HCFO-1224yd(Z) under the SNAP program and its current status as an approved substitute, EPA should determine that contribution to stratospheric ozone depletion is not an issue with respect whether the compound may be considered to be VOC-exempt.

B. Contribution to Climate Change

Two aspects of HCFO-1224yd(Z) ensure that approval of a VOC petition is consistent with EPA's previously stated goal of reducing the use of higher global warming potential ("GWP") substances in connection with its review of VOC delisting petitions. First, the GWP of HCFO-1224yd(Z) is approximately 1, or about the GWP of carbon dioxide over 100 years.[18] In addition, as noted above, HCFO-1224yd(Z) will be produced and utilized in refrigeration equipment that is currently subject to EPA regulations constraining venting and release.[19] This constrained use will serve to minimize any impact on climate change.

Second, the GWP of HCFO-1224yd(Z) is comparable to or lower than other substitutes. EPA has noted that "[f]or centrifugal and positive displacement chillers, R-1224(Z)'s GWP of about 1 is comparable to or lower than that of other acceptable substitutes such as, for new chillers, ammonia absorption, carbon dioxide (CO), and hydrofluoroolefin (HFO) 1336mzz(Z), and for new and retrofit chillers, R-450A and R-513A, with GWPs ranging from 0 to 630."[20] In industrial process refrigeration, HCFO-1224yd(Z) is also comparable to or lower than other acceptable substitutes that have GWPs ranging from 0 to 14,800.[21] Thus, the GWP impact of HCFO-1224yd(Z) poses no barrier to EPA's approval of VOC exempt status.

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[15] 70 Fed. Reg. at 54,050-1.

[16] *Id*.

[17] For example, n-Propyl Bromide used in solvent cleaning was approved under SNAP where emissions in the United States were estimated to have an ODP of approximately 0.012-0.018. 72 Fed. Reg. 30,142, 30,146 (May 30, 2007).

[18].84 Fed. Reg. at 64,766.

[19] See *supra*, n. 13.

[20] 84 Fed. Reg. at 64,767.

[21] *Id*.

D. Toxicity

EPA's Office of Pollution Prevention and Toxics (OPPT) evaluated the available toxicity data for HCFO-1224yd(Z) as part of its review of the premanufacture notification (PMN) submitted for the substance (P-17-295) under the Toxic Substances Control Act (TSCA). As set forth in the TSCA Section 5(e) consent order for this PMN, EPA has determined, based on the results of a 90-day inhalation study, that the No Adverse Effects Concentration (NOAEC) for HCFO-1224yd(Z) is 10,000 ppm.

IV. Conclusion

EPA may approve HCFO-1224yd(Z) as VOC exempt based on all the parameters that EPA has considered when granting similar exemptions over the past 40 years. HCFO-1244yd(Z) incremental reactivity is considerably below that of ethane and use of the substance is very unlikely to contribute to ozone formation in any meaningful fashion. HFCO-1244yd(Z) also addresses all other criteria and considerations that EPA has evaluated for VOC exemptions related to ODP, GWP and toxicity. Thus, there are no factors which should preclude EPA from acting on the basis of the information provided in this petition to approve HCFO-1224yd(Z) as VOC exempt.